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Restructuring of silica supported vanadia during propane oxidative dehydrogenation studied by combined synchrotron radiation based *in situ* soft X-ray absorption and photoemission

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ABSTRACT

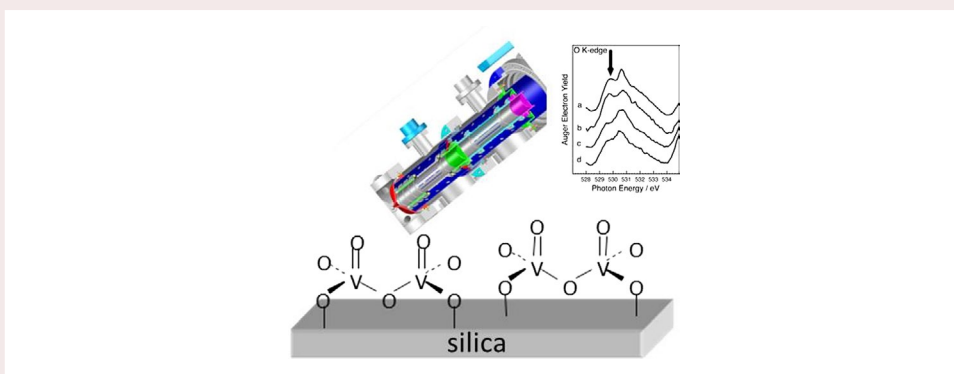
A series of vanadia catalysts supported on mesoporous silica SBA-15 has been prepared with a loading in the range of 2–14 wt-% V and characterized under oxygen and propane oxidative dehydrogenation reaction conditions at elevated temperature up to 550 °C. *In situ* soft X-ray absorption spectra at the vanadium L- and oxygen K-edges and *in situ* synchrotron based X-ray photoemission spectra reveal a restructuring of vanadium species that results in an enhanced degree of dispersion of molecular vanadia species on the silica support. The impact of the X-ray beam on the XAS spectra of dispersed V_xO_y species has been studied and a brief perspective of X-ray based electron spectroscopy as a probe in catalyst characterization is given.

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Vanadia; oxidative dehydrogenation (ODH); *in situ*; dynamic surface restructuring; near edge X-ray absorption spectroscopy (NEXAFS); ambient pressure X-ray photoemission (AP-XPS)




Introduction

Vanadium in its highest oxidation states 4+ and 5+ is an important component of industrially relevant oxidation catalysts, such as alkali-promoted silica-supported vanadium pyrosulfate for the oxidation of SO_2 to SO_3 [1], vanadyl pyrophosphate $(VO)_2P_2O_7$ for the oxidation of *n*-butane to maleic anhydride [2], vanadia-titania catalysts for oxidation of *o*-xylene to phthalic anhydride [3] and promoted mixed MoV oxides for the oxidation of acrolein to acrylic acid [4]. *In situ* studies of oxidation catalysts underline the importance of a thin 2-dimensional surface layer that forms under operation [5,6] or during synthesis [7]. The surface layer contains the active element in a concentration and coordination that differs

from the bulk of the catalyst. However, it is difficult to resolve the molecular structure of the minor active surface species in presence of the majority of similar species in the crystalline bulk. Two-dimensional vanadium oxide anchored on highly ordered mesoporous silica (V_xO_y/SiO_2) serves as model system to investigate differences in the reactivity of the individual surface metal oxide species [8–10]. One test reaction is the oxidative dehydrogenation of propane. The structure of the vanadium oxide species on the freshly prepared catalyst changes with the loading [11,12], but the dynamics of such surface species under reaction conditions of propane oxidation are unknown. The aim of the present study was to analyze whether the V_xO_y/SiO_2 can be considered as a static system or whether dynamic changes

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in the degree of oligomerization have to be considered under reaction conditions of propane oxidation.

Synchrotron based *in situ* near edge X-ray absorption fine structure (NEXAFS) measurements and *in situ* X-ray photoelectron spectroscopy (XPS) have been applied to study details of the electronic surface structure. Interaction of molecular species with the brilliant X-ray beam can modify the chemical state and structure of these species. Hence, we have also studied the effect of the X-ray beam on highly dispersed vanadium oxide species. A composite catalyst based on vanadium oxide (V_xO_y) deposited on multiwall carbon nanotubes (MWCNT) has been synthesized and studied by $V L_3$ -NEXAFS. MWCNT with their inherent electronic conductivity avoid adding extra complexity of applying electron spectroscopy to non-conductive supports like silica. Furthermore, carbon supported V_xO_y composite materials are promising alternative catalysts for styrene production.

Experimental

Catalyst preparation

The samples selected in the present study are composed of highly dispersed vanadium oxide supported on mesoporous silica (SBA-15) and vanadium oxide nanoparticles supported on multiwall carbon nanotubes (MWCNT).

Vanadium oxide supported on MWCNT was synthesized by atomic layer deposition (ALD). The MWCNT (Shandong Dazhang Nano Materials Co.) were treated with nitrosulfuric acid to produce oxygen containing functional groups on the surface that serve as reactant with the vanadium precursor. In brief, 10 g of MWCNT were mixed with 500 mL acid, heated up to 105 °C and stirred for 4 h. The intensively washed MWCNT were dried in a vacuum-oven at 80 °C for 12 h to eliminate remaining water.

Gas phase deposition of vanadium oxide on the functionalized MWCNT was performed with Vanadium(V) oxytriisopropoxide (Sigma-Aldrich, CAS: 5588-84-1) as precursor in a commercial ALD from Ultratech (Savannah S200). The base pressure during the deposition and drying process at 150 °C varied between 26 and 30 Pa. Vanadium(V) oxytriisopropoxide was heated up to 70 °C and pulsed for 0.5 s, and remaining for 40 s in the reaction chamber with the MWCNT support material. After 40 s the chamber was purged for 30 s with a 20 sccm argon flow to remove remaining vanadium precursor until the base pressure was reached. This procedure was repeated 1000 times to create a maximum loading of dispersed vanadium oxyisopropoxide species on the MWCNT surface. A higher number of preparation loops did not increase the vanadium loading further as it has been confirmed by atomic absorption spectroscopy. The sample was located for additional 2 h at 150 °C inside

the chamber with a continuous argon flow of 20 sccm to reduce adsorbed or rather not bonded vanadium species. The amount of deposited vanadium was determined to 5 wt-% via atomic absorption spectroscopy. The sample was annealed in a mixture of 9 vol.% oxygen in argon for 30 min at 300 °C.

SBA-15 was synthesized based on a recipe of Zhao and co-workers [13,14]. The vanadium loading of the V_xO_y /SBA-15 catalysts was varied in the range 2–14 wt-% designated as 2V–14V. Detail description of the catalyst synthesis as well as catalyst characterization is given in Gruene et al. [8] and Hamilton et al. [9].

In situ NEXAFS spectroscopy and *in situ* XPS

In-situ near edge X-ray absorption fine structure (NEXAFS) measurements and *in situ* X-ray photoelectron spectroscopy (XPS) have been carried out at the synchrotron radiation facility BESSY II of the Helmholtz-Zentrum Berlin, Germany (HZB) using monochromatic radiation of the ISSS (Innovative Station for In Situ Spectroscopy) beamline as a tunable X-ray source. Soft X-ray absorption and XP spectra were measured in vacuum, in the presence of oxygen or the feed containing propane and oxygen in a molar ratio of 2:1 (total flow 6 sccm) at elevated temperature using the high pressure station designed and constructed at the Fritz-Haber-Institut, Berlin. Details of the setup are described elsewhere [15–17]. The catalyst powders have been pressed into self-supporting discs (1 ton, 8 mm diameter). NEXAFS spectra of the dehydrated samples have been obtained in 50 Pa O_2 at 400 °C and a mixed flow of 4 sccm C_3H_8 and 2 sccm O_2 at a total pressure of 50 Pa at 400 °C, 500, and 550 °C by heating the material *in situ* in the spectroscopy cell with 5 °C/min up to the final temperature. Oxygen K-edge excitation spectra have been recorded in the Auger electron yield mode by operating the electron spectrometer with a pass energy of 100 eV as a X-ray absorption spectroscopy (XAS) detector to minimize contributions from the gas phase to the spectra. O K-edge spectra of the sample surface have been corrected for the remaining effects of O_2 gas phase absorption following a procedure developed in our group [18]. In order to increase the signal to noise ratio a data reduction by a factor 2 has been applied to the raw spectra (containing about 1000 points per scan) by averaging adjacent points. Three scans have been averaged and the X-ray spot position on the sample has been changed after each scan to minimize damage of the surface by the brilliant synchrotron X-ray beam. Absolute energy calibration has been achieved by setting the π^* resonance of the O_2 gas phase signal to 530.9 eV and the spectral resolution was about 150 meV. Further details of the metrology and data treatment are presented elsewhere [18].

Si 2p, O 1s and V 2p XPS core level spectra have been obtained at elevated temperature by setting the

pass energy of the spectrometer to 20 eV. The photon energy was 680 eV for O 1s/V 2p spectra and 255 eV for Si 2p spectra, respectively. Binding energy calibration has been done by setting the peak of Si 2p of the SBA-15 support to 103.6 eV as reported in the literature [19–21]. For determination of the V/Si atom abundance ratio the XPS spectra were normalized by the storage ring current and by the photon energy dependent incident photon flux, which was measured prior to the experiments using an Au foil. The photon flux obtained was corrected for higher diffraction orders that contribute only to the background but not to the peak intensity in XPS. Quantitative element abundance calculations were performed using CASA data analysis software evaluating normalized core level intensities taking into account the photon energy dependence of the atomic sub-shell photo-ionization cross sections [22,23].

A gas chromatograph (VARIAN CP4900 μ -GC) has been attached to the spectroscopic cell to analyze the composition of the effluent gases.

Results and discussion

V L₃-NEXAFS of V_xO_y/MWCNT

The impact of the X-ray beam has been studied by measuring V L₃-X-ray absorption spectra (corresponding to transition from V 2p to V 3d orbitals) of vanadium oxide nanoparticles dispersed on multiwall carbon nanotubes. Figure 1 shows the sequence of spectra taken on the very same spot for every scan in vacuum at room temperature. The X-ray exposure time for every scan is 247 s and the photon flux can be estimated to around $1.4 \cdot 10^{11}$ photons/s delivered in a X-ray spot size of about $150 \times 100 \mu\text{m}$. The first spectrum of the sequence (black curve) shows pronounced resonances with the peak maximum at around 519.5 eV. The spectral shape resembles the spectrum of V₂O₅ (Figure 2(A)) suggesting that the local, first shell structure surrounding the absorbing vanadium atom features some typical properties of vanadium pentoxide. Further exposure to soft X-rays during every following scan results in less pronounced features and in a shift of the overall peak position to lower photon energies. Shape and position of the V L₃-edge XAS spectrum suggests that the initial state of the catalyst is in a V⁵⁺ state while exposure to X-rays in vacuum results in a rather fast reduction towards V⁴⁺ species as deduced from the downshift of the spectrum to lower photon energies [10,24]. The less well-defined spectral shape of the V L₃-edge reveals that a mixture of vanadium oxidation states with V⁵⁺, V⁴⁺ and possibly also a minor amount of V³⁺ components is present. Hence, X-ray beam induced reduction in vanadium oxidation state going along with a modification of the structure of the vanadia species needs to be taken into account when studying highly dispersed V_xO_y species, in particular in vacuum. Care has been taken in the following

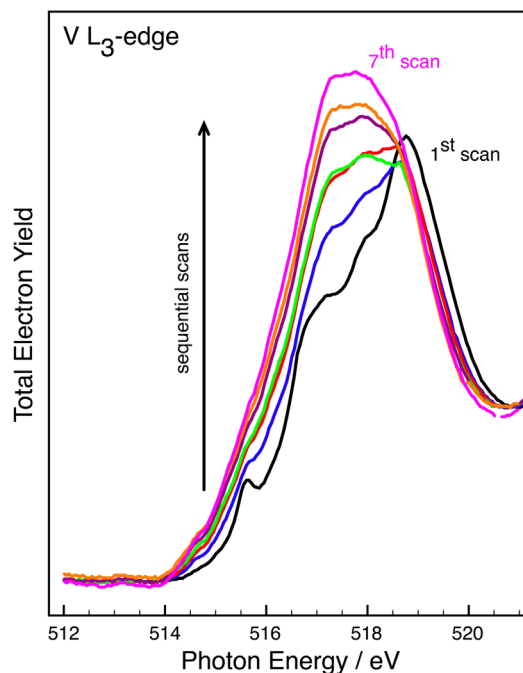


Figure 1. The evolution of V L₃ NEXAFS of the V_xO_y/MWCNT catalyst during sequential scans in vacuum at room temperature is shown. Every new scan adds 247 s of X-ray exposure.

study of V_xO_y on silica to keep X-ray exposure times short by varying the beam position on the sample after every scan. Also, exposing the catalysts not to vacuum but to an oxidative gas environment prevents rapid X-ray induced reduction.

In situ NEXAFS and XPS of VxOy/SBA-15

X-ray photoelectron spectroscopy is well established among the electron spectroscopy techniques to gather information about atom abundance and dispersion of supported metal particles, see Venezia et al. and references therein [25]. Unfortunately, low metal loading on insulating supports like SiO₂ often prevent the recording of high quality XP spectra due to differential charging. This effect is even more pronounced when using high brilliant monochromatic X-ray sources like a synchrotron beam for excitation. Also in this work, reasonable XP spectra were obtained only at high loading of 14 wt-% vanadium at elevated temperature. These X-ray photoelectron core level spectra will be discussed later. Figure 1S in the supplemental material gives survey XPS scans for low loading catalysts and at lower temperature for 14V exemplifying the effect of differential charging like shift of all core level peaks to higher apparent binding energy, peak broadening, peak splitting and development of asymmetric peak shapes that does not allow a reliable XPS peak analysis. To study the evolution of the vanadium oxide species under different reaction conditions for catalysts with lower transition metal oxide content, we analyzed the near edge structure of the X-ray absorption spectra (NEXAFS). Figure 2 presents

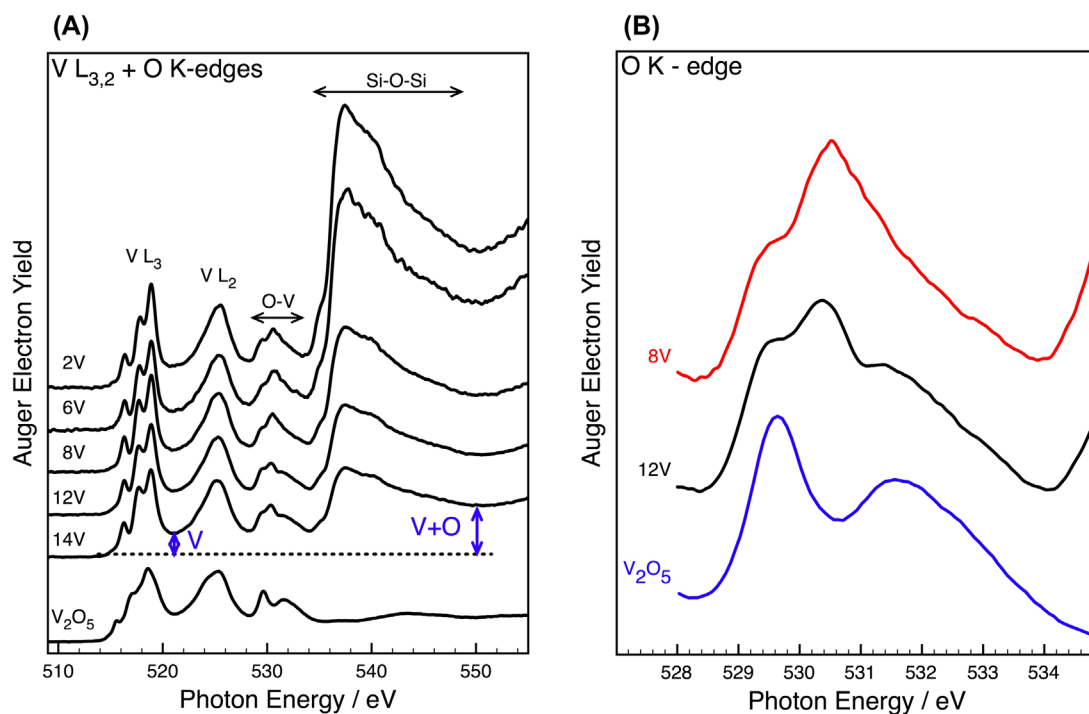


Figure 2. (A) presents the V L_{3,2}- and O K-NEXAFS of dehydrated VO_x/SBA-15 catalysts with various V loadings as indicated. Spectra have been recorded in 50 Pa O₂ at 400 °C. A reference spectrum of V₂O₅ powder is shown as well. The photon energy regions for V L₃-, V L₂- NEXAFS and the O K-edge absorption dominated by O–V and Si–O–Si bonds, respectively, are indicated. The determination of the vanadium edge jump “V” and the total edge jump “V + O” are marked with arrows (details in the text). In (B) a detail of the O K-NEXAFS is presented for a high loading (12 V) and low loading (8 V) catalyst and compared to the O K-NEXAFS of bulk V₂O₅. Spectra are offset for clarity.

the NEXAFS of dehydrated V_xO_y/SBA-15 catalysts with various vanadium loading recorded in presence of 50 Pa O₂ at 400 °C and compared to a reference spectrum of bulk V₂O₅. In Figure 2(A) the V L_{3,2} absorption spectra (corresponding to transition from V 2p to V 3d orbitals) characterized by absorption peaks in the photon energy range between 512 and 528 eV followed by the oxygen K-edge (transition from O 1s to O 2p) above 528 eV are shown. The spectra have been normalized to the same vanadium edge jump (indicated as “V” in Figure 2(A)), i.e. to the same number of absorbers i.e. to the same vanadium amount. A comparison of the V L₃-NEXAFS of vanadia supported on silica with quantum chemical calculations can be found in recent literature [10]. The O K-edge feature in the energy range between 528 and 534 eV are determined by peculiarities of the V–O bonding while resonances at photon energy above approximately 534 eV reflect mainly the O 1s excitations of Si–O–Si bonds, i.e. of the support material SBA-15 as explained in great detail in the literature [26]. The varying intensity ratio of the vanadium NEXAFS relative to the oxygen related NEXAFS in Figure 2(A) reflects directly the different V loading of the catalysts. Restricting a detailed data evaluation on the energy range that serves as a fingerprint for V–O bonds (528–534 eV) reveals a similar spectral O K-edge shape on the one hand for a V loading of 12 and 14 wt-% and on the other hand of catalysts with a vanadium loading of 8 wt-% V and below (Figure 2(A)). Details of the O K-NEXAFS in this

photon energy range of 8 and 12V are compared with the spectrum of V₂O₅ in Figure 2(B). As deduced in a recent work by comparison of experimental with theoretical spectra obtained by *ab initio* DFT calculations the shape of the O K-NEXAFS of the dehydrated catalysts shown in Figure 2(B) with a V loading of 8 wt-% and below on SBA15 suggests the presence of both monomeric and polymeric species [26]. The O K-edge spectrum of 12 and 14V show a more pronounced shoulder at 529.5 eV and about 531.6 eV (Figure 2(B)) as the lower loading catalysts. Obviously, these parts of the spectra resemble the characteristic features of V₂O₅. However, the overall spectral shape is still different from bulk V₂O₅. Hence it can be concluded that the geometric arrangement of V species in highly loaded catalysts is not the same as in V₂O₅ but possesses only some specific features of the V₂O₅ bulk structure. Based on this observation it seems reasonable to assign some three-dimensional character to V species with a metal loading equal and above 12V while at V loadings of 8 wt-% and below this character is missing although V–O–V bonds (2-dimensional vanadium oxide polymers) are present [10,26].

The sudden, step-like increase of the X-absorption intensity (edge jump) is proportional to the amount of absorbing atoms and therefore a measure of the element abundance as mentioned above [24]. The increase in intensity due to continuous absorption is typically buried by the strong intensity increase due to resonant absorption (bound–bound transition) in the soft energy

range. Therefore, it is usually not possible to extract absolute abundance numbers but relative changes can still be evaluated. In this work we make an attempt to quantitatively analyze the XAS edge intensity. The intensity at about 522 eV (indicated as “V” in Figure 2(A)) after subtraction of the pre-edge intensity was taken as a measure of the vanadium abundance. Silica does not show any absorption feature in this energy range. Intensity “V + O” in Figure 2(A) (at about 548 eV) is the total edge jump that represents vanadium plus all oxygen absorbers. Since the overwhelming part of oxygen is bound to non-reducible silica support this is indeed a good measure for the V + Si abundance. The evolution of the vanadium to total edge jump ratio ($V/V + O$), related to the $V/V + Si$ abundance ratio, is shown in Figure 3(a) for the 6, 8, and 14V catalysts in O_2 after dehydration and in a mixture of C_3H_8 and O_2 (2:1) below reaction temperature and at temperatures at which the catalyst produces propylene. An increase in the edge jump ratio that corresponds to an increase in the V to SiO_2 support ratio suggests an increase in dispersion as it is in the case of XPS methodology [25]. In this view, the increase of the intensity ratio of catalysts (6 and 8 V) with lower loading during dehydration (heating from 25 to 400 °C in O_2) suggests that the dispersion of vanadium oxide species is improved during this treatment. The abundance/dispersion of vanadium seems to remain constant under ODH reaction conditions at 500 °C for 6V while there is a further slight increase for 8V that decreases again when heating further to 550 °C. In presence of the feed at 550 °C, propane conversions of approximately 0.2% and propylene selectivity of 56% were measured in the effluent gas of the *in situ* XPS cell by gas chromatography. The low conversion is attributed to the batch-reactor-like design of the *in situ* spectroscopy cell.

The most pronounced effect in the edge jump ratio was observed for the high loading catalyst 14V with a

strong decrease in intensity ratio when applying ODH reaction conditions. Obviously, some of the vanadium species become not further accessible to be probed by low kinetic electrons after excitation with soft X-rays. Albeit sublimation of vanadium oxide cannot be excluded under the reduced pressure at the high reaction temperature, re-distribution of vanadium oxide on the mesoporous silica support seems to be more likely an explanation for the observed phenomenon. Although there was no clear indication of three-dimensional (bulk-like) vanadia by UV-vis spectroscopy in the as synthesized, dehydrated catalyst, vibrational resonances at 144, 284, 303, 404, 482, 525, 702 and 994 cm^{-1} visible in the Raman spectrum of 14V suggested the presence of 3D vanadium oxide particle traces before catalysis [8]. This is in agreement with the O K-NEXAFS presented in Figure 3(B), (spectrum a). Interestingly, the vanadium abundance on the outermost surface as determined by NEXAFS is similar for all three catalysts under ODH reaction conditions irrespective of the difference in the formal V loading during preparation. This suggests a comparable V spreading on the outermost surface for the high loading catalyst, i.e. an apparent transformation of the traces of bulk-like vanadium oxide nano-particles into 2-D vanadium oxide species in the feed at reaction temperature, which is also in accordance with the catalytic properties of the 14V catalyst [8].

The details of the O K-NEXAFS, as presented in Figure 3(B), support the interpretation that the remarkable evolution in vanadium abundance for 14V goes along with structural modifications. The intensity of the resonance at 529.6 eV (marked with an arrow in Figure 3(B)) is significantly reduced when the catalyst is heated from 400 (spectrum b) to 500 °C (spectrum c) under ODH reaction conditions. As discussed before when analyzing the O K-NEXAFs of catalysts with different V loading (Figure 2(B)), this is an indication of

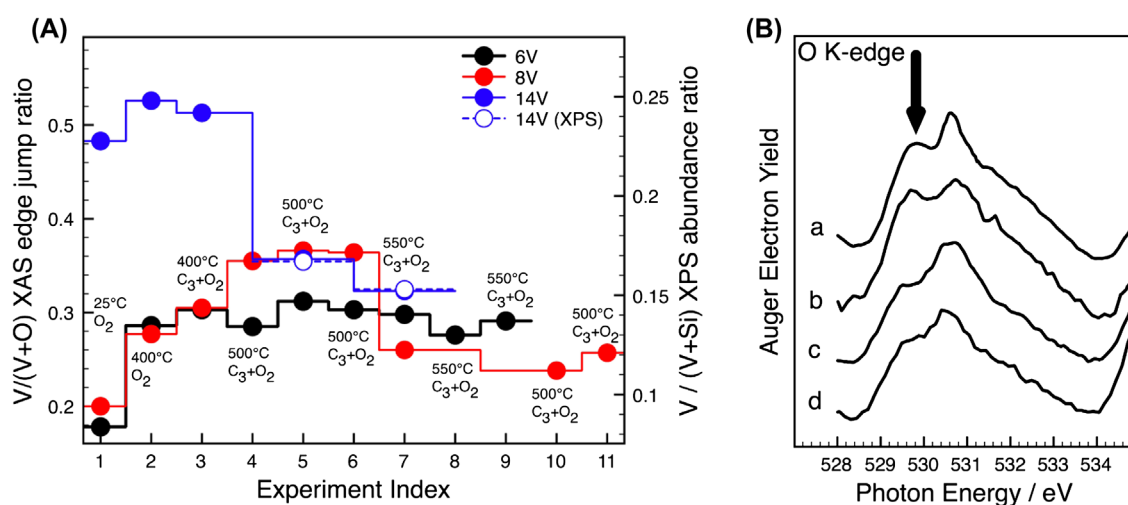


Figure 3. In (A) the evolution of the V-edge/total edge jump ratio (corresponding to the intensity ratio $V/(V + O)$ as indicated in Figure 2(A)) is shown for three different vanadium loadings (6, 8, and 14 wt-% V) at different reaction conditions as designated in the Figure. The $V/(V + Si)$ atom abundance ratio as determined by XPS for the 14V catalysts is included. (B) shows the evolution of a detail of the O K-edge for the 14V catalysts at O_2 , 400 °C (a), $C_3H_8 + O_2$ (2:1), 400 °C (b), $C_3H_8 + O_2$ (2:1), 500 °C (c), and $C_3H_8 + O_2$ (2:1), 550 °C (d).

a loss of 3-dimensional character of the surface vanadium oxide species, i.e. a spreading of the remaining vanadium species on the outer surface. The resulting O K-NEXAFS under ODH reaction conditions (spectrum c and spectrum d in Figure 3(B)) resembles the spectra found for lower V loading (i.e. ≤ 8 wt-% V) catalyst (compare to Figure 2(B)). Therefore, it can be concluded that these catalysts are structurally similar under ODH reaction condition. The structural dynamics observed in particular for the 14V catalyst are in good agreement with the results of kinetic studies in a fixed bed reactor under ambient pressure [8]. Whereas the low loaded catalysts show a quite stable and reproducible performance in repeated experiments, the activation energy measured for fresh 14V upon determination of the propane conversion between 380 and 450 °C was very high (165 kJ mol^{-1}), but drops to 140 kJ mol^{-1} when the determination of the activation energy was repeated a second time. The final value lies close to the activation energy measured for the lower loaded catalysts. The kinetic results in Gruene et al. have been tentatively ascribed to dynamic changes of the catalyst surface structure under operation [8]. The NEXAFS results in the present work provide a rational explanation for the lining-up of activation energies for silica-supported catalysts with different vanadium oxide loading.

As mentioned before, XP spectra sufficient for quantification could only be obtained for 14V at elevated temperature (500 and 550 °C). The $V/(V + \text{Si})$ abundance ratio as revealed by XPS is included in Figure 3(A). (open blue circles). An attempt was made to calibrate the X-ray absorption edge jump data to element abundance data via adjusting the XAS data points by an appropriate scaling to match the XPS data. Although the absolute error bar of the XAS V/Si abundance ratio obtained in this way might be significant due to the limited amount of XPS adjustment values this procedure is sufficient to get an idea about the effect.

In situ $V2p_{3/2}$ XP spectra have been analyzed to determine directly the vanadium oxidation state under ODH reaction conditions. As discussed before, differential charging was sufficiently reduced only on the high vanadium loading catalyst 14V at elevated temperatures as deduced from the undistorted, symmetric $\text{Si}2p$ peak shape of SiO_2 support. Figure 1S in the supplemental material gives survey XPS scans for low loading catalysts and at lower temperature for V14 exemplifying the differential charging. A shift of the apparent binding energy of all core levels and asymmetric peaks shapes were observed both for the high loading catalyst V14 at temperatures below 500 °C (Figure 1S (A)) and for low loading catalysts 6 and 8V at a temperature of 500 °C (Figure 1S (B)). These effects do not allow a reliable analysis of the XPS core level spectra for low loading catalyst or at low temperature. Figure 4(A) and (B) depict the deconvolution of the $V2p_{3/2}$ core level in reaction mixture of propane and oxygen at 500 and 550 °C, respectively. Under these conditions a propane conversion of approximately 0.2% was measured by the gas chromatograph attached to the *in situ* chamber. Three mixed Gaussian/Lorentzian fit profiles centered at 518.7, 517.5 and 516.4 eV binding energy (BE) have been used for peak deconvolution recorded at 500 °C, while only one peak was observed at 550 °C. Possibly, there is a contribution of a peak at lower binding energy at 550 °C as well but it has been omitted in the fit due to uncertainties in peak shape of the fit profile and background subtraction. The contribution of this possible peak at low BE was estimated to be below 4%. The abundance data of these components can be found as Table 1. The XPS peaks at 517.5 eV and 516.4 eV can readily be assigned to V^{5+} and V^{4+} species since the absolute BE, and in particular the BE difference of $\Delta E = 1.1$ eV, agrees reasonably well with literature [27]. The peak centered at 518.7 eV is characteristic for highly dispersed V^{5+} species as discussed in detail in Hess et al. [19]. It can be concluded

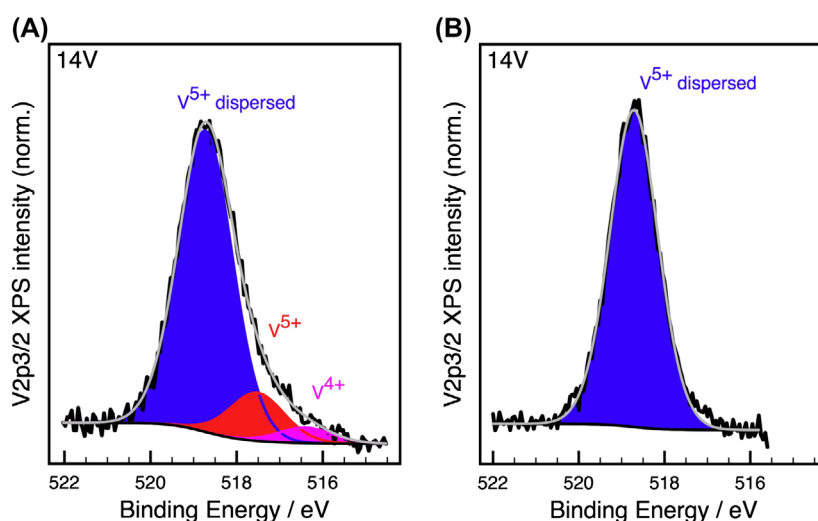


Figure 4. $V2p_{3/2}$ XP core level spectra in ODH reaction mixture ($\text{C}_3\text{H}_8 + \text{O}_2$, 2:1) of (A) 14V at 500 °C, (B) 14V at 550 °C. Note: The deconvolution of the peak into components representing the species V^{5+} “dispersed” (blue), V^{5+} (red), and V^{4+} (magenta) is shown as well.

Table 1. V species abundance as determined by XPS.

Catalyst	Species	Abundance (%)
14V, ODH at 500 °C	V ⁵⁺ "dispersed"	78
	V ⁵⁺	17
	V ⁴⁺	5
14V, ODH at 550 °C	V ⁵⁺ "dispersed"	>96
	V ⁵⁺	<4

that vanadium is present predominantly in its highest oxidation state 5+ as a well dispersed species on the SBA-15 support. This is in a good agreement with the NEXAFS data presented before, *in situ* UV–vis results as well as with results reported in the literature also for other supports [28–32].

Conclusions and future methodology outlook

Vanadia supported on SBA-15 undergoes significant structural surface reconstructions under reaction conditions resulting in highly dispersed species. It has been shown that *in situ* NEXAFS in the soft energy range and *in situ* XPS are valuable tools for the structural characterization of supported metal oxide clusters complementary assisting other methods. Care has to be taken when studying highly dispersed vanadia species with X-rays, in particular in vacuum, since beam induced reduction in vanadium oxidation state going along with a modification of the structure of the V_xO_y species can emerge and tamper the results. Similar effects are expected to happen with powerful lab X-ray sources used in modern XPS set-ups.

Soft X-ray based electron spectroscopy is attractive for catalyst characterization due to its inherent surface sensitivity, high chemical specificity and its capability for element abundance quantification. However, the application of low kinetic energy electrons as a probe in *in situ* X-ray photoelectron spectroscopy does suffer from the strong inelastic scattering of the electrons in the gas phase and sets certain limitations exploiting this methodology in the study of solid-gas and solid-liquid interfaces. Advances in extending the pressure limit are related to the optimization of highly efficient detection systems (like time of flight electron spectrometer) and mainly in ways to decrease the electron scattering either by decreasing the electron path in the gas or liquid, respectively, or by decreasing the electron scattering cross section. An option to minimize the electron path length is the construction of reaction cells that are sealed with electron transparent membranes to confine the high pressure region. It has been shown that graphene is suitable to be both mechanical stable and highly transparent for low kinetic electrons [33–35]. Another possibility to facilitate *in situ* XPS to study solid-gas and solid-liquid interfaces is the decrease of the electron scattering cross section by increasing the kinetic energy of the photoelectrons [36]. This requires the use of sources delivering high photon energies in the tender and hard X-ray regime with a high photon flux due to the low ionization cross sections.

X-ray absorption spectroscopy in the total electron yield mode does not require unscattered electrons since the signal is recorded irrespective of the kinetic energy of the electrons. The absorption of soft X-rays in the gas phase/liquid phase requiring short photon paths to the sample and the signal to background ratio are more important limiting factors that hinder using high pressures for soft XAS in TEY mode. Examples for the application of this methodology can be found in recent literature [37,38].

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Disclosure statement

No potential conflict of interest was reported by the authors.

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